CHANGE OF THE IONIZATION OF SALTS IN ALCOHOLIC SOLVENTS WITH THE CONCENTRATION

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The deviation of largely ionized substances, even in fairly dilute solution, from the mass-action law, and in general from the behavior of perfect solutes, has been the subject of extended discussion among physico-chemical investigators. Evidence is accumulating that at sufficiently small ion-concentrations these substances become normal in their behavior. Thus Kraus and Bray[1] showed that uniunivalent salts dissolved in liquid ammonia and in certain organic solvents conform to the mass-action law when the concentration of the ions in the solution lies below about 0.0001 normal in ammonia, 0.0005 normal in organic solvents; and Arrhenius[2] has made recalculations with the data of Kohlrausch and Maltby on the conductance of aqueous solutions of sodium chloride and nitrate which indicate that these salts behave as perfect solutes in water at concentrations between 0.00002 and 0.0002 normal.

A great variety of expressions have been proposed to account for the deviations at higher concentrations. Of these the one which is most generally applicable is that proposed by Kraus and discussed fully by Kraus and Bray.[3] Kraus and Bray have shown that the conductance of almost any uniunivalent solute in any solvent from the concentration zero up to a fairly high concentration (one where the change in the viscosity of the solution becomes an important factor) can be expressed by an equation of the form:

$$\frac{(c\gamma)^2}{c\,(1-\gamma)} = K + D\,(c\gamma)^m.$$

In this equation K, D, and m are empirical constants which vary with the nature of the solute and of the solvent and with the temperature, and γ represents the equivalent-conductance ratio Λ/Λ_0. This expression evidently requires that any solute in any solvent conform to the mass-action law at sufficiently small concentrations, when the term $D(c\gamma)^m$ becomes negligible.

The present investigation on the conductance of sodium iodide and ammonium iodide in isoamyl alcohol and of sodium iodide in propyl alcohol was undertaken for two purposes: primarily, in order to determine whether in these solvents, somewhat similar in nature to water,

salts conform to the mass-action law at very small concentrations; and secondarily, to test further the applicability of Kraus' empirical equation throughout the fairly wide range of concentration employed in our work. Dutoit and Duperthuis[4] have already studied solutions in these alcohols, but it seemed desirable ro extend and confirm their results.

For the conductance measurements a new form of cell was constructed which enabled them to be made in a vacuum, entirely out of contact with air, which exerts a slow oxidizing action. The specific conductance of the purified alcohols employed was about 2×10^{-8}.

Several series of measurements at 25° were made with each kind of solution. The equivalent conductances were plotted against the logarithms of the concentrations on a large-scale plot, a representative curve was drawn through them, and values of the equivalent conductance were accurately read off at various round concentrations. These values are presented in Table 1 under the heading 'Λ obs;' the concentrations in milliequivalents per liter of solution being given under the heading 10^3c.

The values of the conductance at zero concentration given in the table and the values of the constants of the Kraus equation were determined by plotting the results in various ways. The constants were found to have the following values, when the concentration is expressed in equivalents per liter:

For NaI in isoamyl alcohol: $10^4K = 5.85; D = 0.374; m = 1.20$.
For NH$_4$I in isoamyl alcohol: $10^4K = 6.93; D = 0.324; m = 1.17$.
For NaI in propyl alcohol: $10^4K = 38.3; D = 0.208; m = 0.75$.

With the help of these constants the equivalent conductances at round concentrations were calculated. These are given in the table under the heading 'Λ calc.'

In the columns of the table which are headed '% diff.' are given the percentage differences between the calculated and observed values, showing the degree of conformity of the results with the requirements of the equation. In the most accurate series, that with sodium iodide in isoamyl alcohol, the maximum difference, even though the conductance passes through a minimum (at 0.1 normal), will be seen to be 1.4% except at the highest concentration (0.400 normal), where the calculated values begin to deviate widely from the observed ones.

The values of $1/\Lambda$ were plotted against those of $c\Lambda$, in order to test their conformity at very small concentrations with the mass-action law, which requires that such a plot be a straight line. The results showed that the mass-action law holds true within the experimental

TABLE 1

OBSERVED AND CALCULATED VALUES OF THE EQUIVALENT CONDUCTANCE

$10^3 c.$	NaI in Isoamyl Alcohol			NH₄I in Isoamyl Alcohol			NaI in Propyl Alcohol		
	Λ obs.	Λ calc.	% diff.	Λ obs.	Λ calc.	% diff.	Λ obs.	Λ calc.	% diff.
0.00	7.79			.7.92			20.10		
0.05	7.182	7.194	+0.17	7.396	7.476	+1.08	(20.11)		
0.10	6.636	6.658	+0.33	7.032	7.105	+1.04	19.65	19.53	−0.61
0.20	6.115	6.142	+0.43	6.256	6.352	+1.54	19.17	19.13	−0.21
0.40	5.307	5.335	+0.53	5.464	5.598	+2.46	18.42	18.49	+0.38
0.80	4.451	4.460	+0.20	4.672	4.794	+2.62	17.38	17.56	+1.03
1.00	4.184	4.183	−0.03	4.408	4.552	+3.03	17.00	17.21	+1.24
2.0	3.394	3.374	−0.61	3.588	3.663	+2.23	15.73	16.03	+1.90
5.0	2.560	2.534	−1.02	2.656	2.676	+0.75	13.62	13.56	−0.44
10.0	2.024	1.995	−1.43	2.168	2.164	−0.19	12.04	11.80	−1.99
20.0	1.649	1.635	−0.69	1.776	1.763	−0.73	10.44	10.31	−1.25
40.0	1.408	1.404	−0.28	1.448	1.456	+0.55	8.90	8.82	−0.90
100	1.294	1.290	−0.31	1.336	1.339	+0.22	7.33	7.26	−0.95
150	1.312	1.309	+0.023	1.332	1.335	+0.22	6.85	6.79	−0.88
200	1.339	1.336	−0.22						
300	1.393	1.400	+0.50						
400	1.413	1.459	+3.20						
500	1.396								

error between the concentrations 0.00005 and 0.0004 normal. At the latter concentration the correction term $D(c\gamma)^m$ in the Kraus equation amounts to only 3.5% of the mass-action constant K in the case of sodium iodide in isoamyl alcohol.

A full description of this work will appear in the June number of the *Journal of the American Chemical Society.*

[1] Kraus and Bray, *J. Amer. Chem. Soc.*, 35, 1354, 1384 (1913).

[2] Arrhenius, *Meddelanden fr. K. Vetenskapakademiens Nobel-Institut*, 2, No. 42, 10 (1913).

[3] Kraus and Bray, *Loc. cit.*, p. 1319.

[4] Dutoit and Duperthuis, *J. chim. phys.*, 6, 699 (1908).